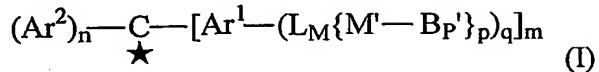


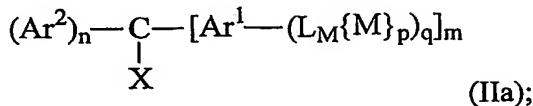
CLAIMS

1. A method of forming an ion of formula (I):

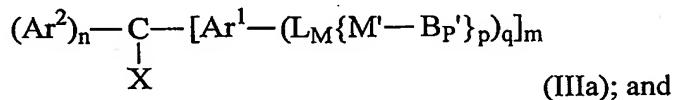


comprising the steps of:

5 (i) reacting a compound of the formula (IIa):



with a biopolymer, B_P , having at least one group capable of reacting with M to form a covalent linkage, to provide a biopolymer derivative of the formula (IIIa):



10 (ii) cleaving the $C - X$ bond between X and the α -carbon atom of the derivative of formula (IIIa) to form the ion of formula (I);

where:

$C\star$ is a carbon atom bearing a single positive charge or a single negative charge;

X is a group capable of being cleaved from the α -carbon atom to form an ion of formula (I);

15 M is independently a group capable of reacting with B_P to form the covalent linkage;

B_P' is independently the biopolymer residue of B_P produced on formation of the covalent linkage;

20 M' is independently the residue of M produced on formation of the covalent linkage;

Ar^1 is independently an aromatic group or an aromatic group substituted with one or more A ;

Ar^2 is independently an aromatic group or an aromatic group substituted with one or more A ;

optionally wherein (a) two or three of the groups Ar^1 and Ar^2 are linked together by one or more L^5 , where L^5 is independently a single bond or a linker atom or group; and/or (b) two or three of the groups Ar^1 and Ar^2 together form an aromatic group or an aromatic group substituted with one or more A ;

25 A is independently a substituent;

L_M is independently a single bond or a linker atom or group;

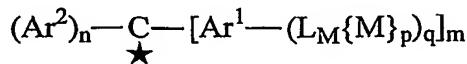
$n = 0, 1$ or 2 and $m = 1, 2$, or 3 , provided the sum of $n+m = 3$;

p independently = 1 or more; and

q independently = 1 or more.

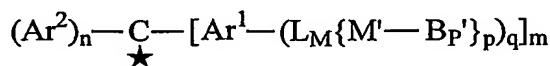
2. A method of forming an ion of formula (I), comprising the steps of:

(i) reacting a compound of the formula (IIb):



5 $X\star$ (IIb);

with a biopolymer, B_p , having at least one group capable of reacting with M to form a covalent linkage, to provide a biopolymer derivative of the formula (IIIb):



$X\star$ (IIIb); and

dissociating $X\star$ from the derivative of formula (IIIb), to form the ion of formula (I);

10 where:

$X\star$ is a counter-ion to $C\star$;

and $C\star$, M, B_p' , M' , Ar^1 , Ar^2 , L_M , n, m, p and q are as defined in claim 1.

15 3. A biopolymer derivative of the formula (IIIa).

4. A biopolymer derivative of the formula (IIIb).

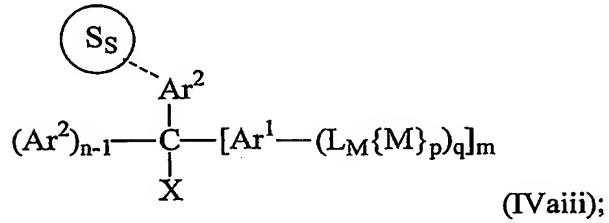
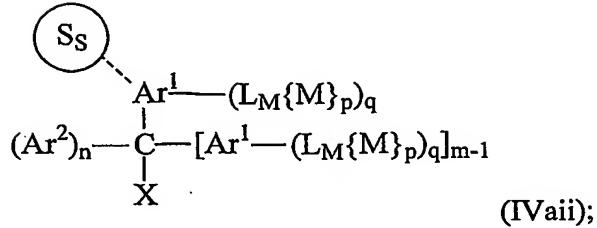
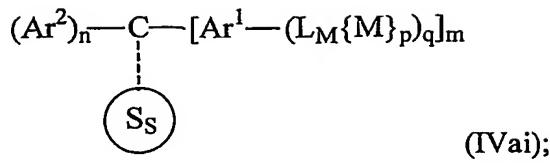
5. An ion of formula (I).

20 6. A compound of the formula (IIa).

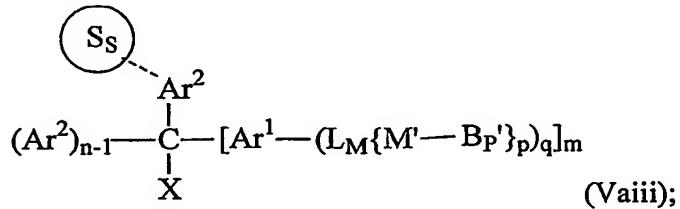
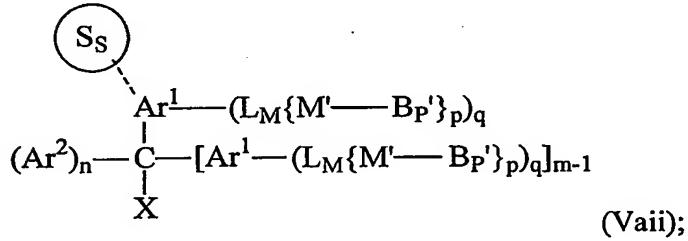
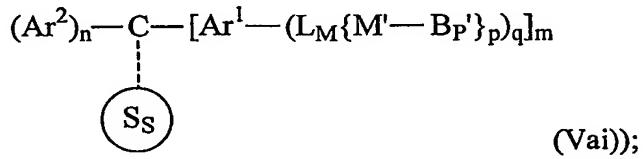
7. A compound of the formula (IIb).

8. A method of forming an ion of formula (I) comprising the steps of:

25 (i) reacting a solid support of formula (IVai), (IVaii), or (IVaiii):



with a biopolymer, B_p , having at least one group capable of reacting with M to form a covalent
5 linkage, to provide a modified solid support of the formula (Vai), (Vaii), or (Vaiii), respectively:



and either:

10 (iia) for modified solid supports of formula (Vai) cleaving the $C-S_s$ bond between
the α -carbon atom of the modified solid support of formula (Vai) and the solid support S_s to form the
ion of formula (I);

(iib) for modified solid supports of formula (Vaii), either simultaneously or sequentially, cleaving the C-X bond between X and the α -carbon atom and cleaving the SS- - -Ar1 bond between the solid support and the Ar1 group to form the ion of formula (I); or

5 (iic) for modified solid supports of formula (Vaii), either simultaneously or sequentially, cleaving the C-X bond between X and the α -carbon atom and cleaving the SS- - -Ar2 bond between the solid support and the Ar2 group to form the ion of formula (I);

where:

X, Ar¹, Ar², B_{P'}, L_M, M', n, m, p and q are as defined in claim 1;

S_S is a solid support;

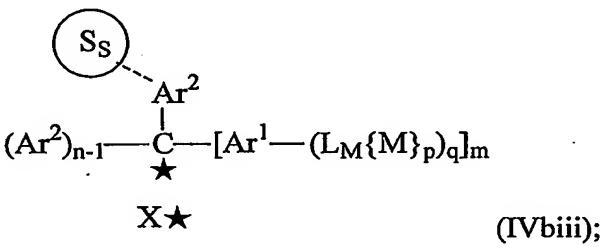
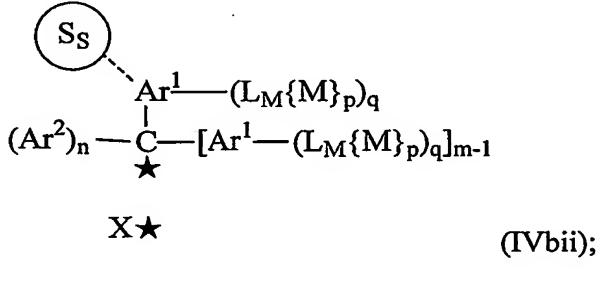
10 C- - -S_S comprises a cleavable bond between C and S_S;

S_S- - -Ar¹ comprises a cleavable bond between Ar¹ and S_S; and

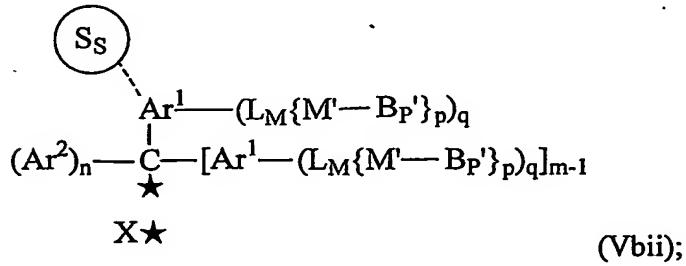
S_S- - -Ar² comprises a cleavable bond between Ar² and S_S.

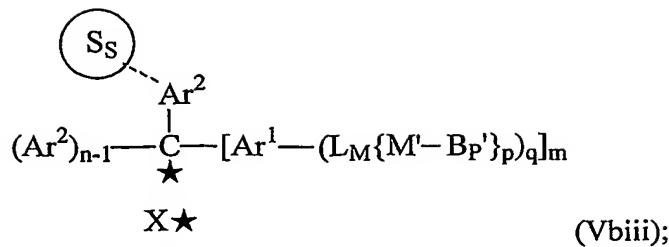
9. A method of forming an ion of formula (I) comprising the steps of:

15 (i) reacting a solid support of formula (IVbii) or (IVbiii):



with a biopolymer, B_{P'}, having at least one group capable of reacting with M to form a covalent linkage, to provide a modified solid support of the formula (Vbii) or (Vbiii), respectively:





and either:

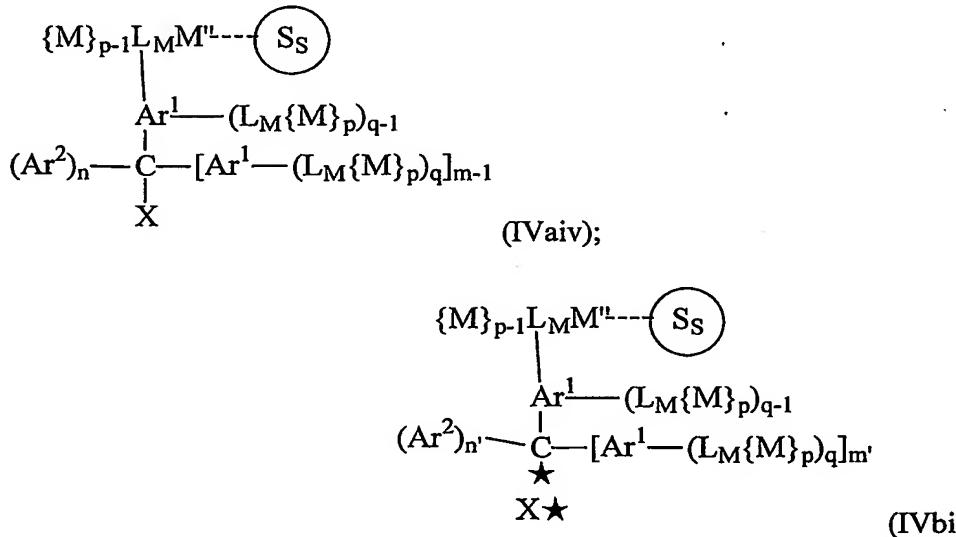
(iia) for modified solid supports of formula (Vbii), either simultaneously or sequentially, dissociating X★ from the derivative of formula (Vbii) and cleaving the Ss- -Ar¹ bond between the solid support and the Ar¹ group to form an ion of formula (I); or

(iib) for modified solid supports of formula (Vbiii), either simultaneously or sequentially, dissociating X★ from the derivative of formula (Vbiii) and cleaving the Ss- -Ar² bond between the solid support and the Ar² group to form an ion of formula (I);

where: X★, Ar¹, Ar², BP', LM, M, M', n, m, p, q, Ss, C- -Ss, Ss- -Ar¹ and Ss- -Ar² are as defined in claim 8.

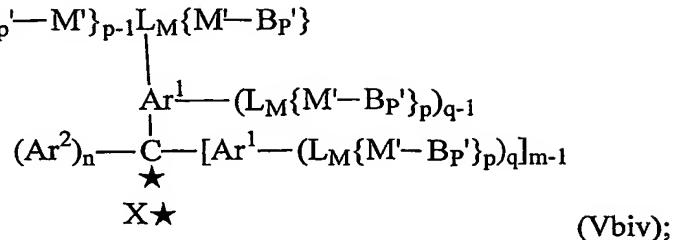
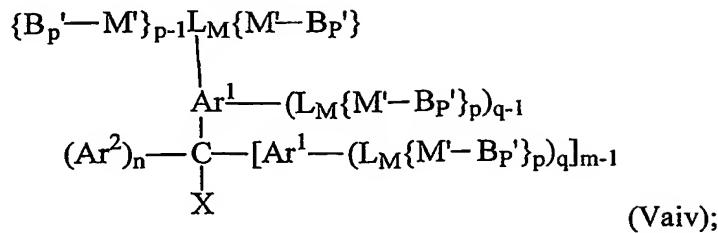
10. A method of forming an ion of formula (I) comprising the steps of:

(i) reacting a solid support of formula (IVaiv) or (IVbiv):



15

with a biopolymer, BP, having at least one group capable of reacting with M to form a covalent linkage, to provide a modified solid support of the formula (Vaiv) or (Vbiv), respectively:



and either:

5 (iia) for modified solid supports of formula (Vaiv), cleaving the C-X bond
 between X and the α -carbon atom to form the ion of formula (I); or

(iib) for modified solid supports of formula (Vbiv), dissociating $X\star$ from the derivative of formula (Vbiv) to form the ion of formula (I);

where:

10 X, $X\star$, Ar^1 , Ar^2 , B_p' , L_M , M, M' , p, q, n, m, and S_S are as defined in claims 8 and 9;

$M'' - S_S$ comprises a bond between M'' and S_S ; and

M'' is the same as M except that S_S is bound to a portion of M which does not form part of M'.

15 11. A solid support of the formula (IVai), (IVaii), (IVaiii), (IVaiv), (IVbii), (IVbiii) or (IVbiv).

12. A modified solid support of the formula (Vai), (Vaii), (Vaiii), (Vaiv), (Vbii), (Vbiii) or (Vbiv).

20 13. A method of any of claims 8-10 or a product of claim 11 or 12 wherein the biopolymer is a synthetic biopolymer.

14. A method or product of claim 13 wherein the synthetic biopolymer is an oligonucleotide, a peptide or a carbohydrate.

15. A method for analysing a biopolymer, B_P , comprising the steps of:

(i) reacting the biopolymer B_P with a compound of formula (IIa) or (IIb) or a solid support of formula (IVai), (IVaii), (IVaiii), (IVaiv), (IVbii), (IVbiii) or (IVbiv);

5 (ii) providing an ion of formula (I); and

(iii) analysing the ion of formula (I) by mass spectrometry.

16. In a method for analysing a biopolymer, B_P , the improvement consisting of: (i) reacting a biopolymer, B_P with a compound of formula (IIa) or (IIb) or a solid support of formula (IVai), (IVaii), (IVaiii), (IVaiv), (IVbii), (IVbiii) or (IVbiv); (ii) providing an ion of formula (I); and (iii) 10 analysing the ion by mass spectrometry.

17. A method of claim 15 or claim 16 wherein the analysis by mass spectrometry is carried out in a spectrometer which is suitable for MALDI-TOF spectrometry.

15 18. A method of any of claims 1, 2, 8-10 or 13-17 or a product of any of claims 3-7, 11 or 12, wherein $C\star$ bears a single positive charge, such that the ions of formulae (I), (IIb) and (IIIb) have the structures:

Formula (I)	$(Ar^2)_n - \underset{\oplus}{C} - [Ar^1 - (L_M - \{M' - B_P'\}_p)_q]_m$
Formula (IIb)	$(Ar^2)_n - \underset{\oplus}{C} - [Ar^1 - (L_M - \{M\}_p)_q]_m$ $X\Theta$
Formula (IIIb)	$(Ar^2)_n - \underset{\oplus}{C} - [Ar^1 - (L_M - \{M' - B_P'\}_p)_q]_m$ $X\Theta$

19. A method of any of claims 1, 2, 8-10 or 13-18 or a product of any of claims 3-7, 11, 12 or 18 20 wherein $n = 2$ and $m = 1$.

20. A method of any of claims 1, 2, 8-10 or 13-19 or a product of any of claims 3-7, 11, 12, 18 or 19 wherein $p = 1, 2$ or 3 .

25 21. A method of any of claims 1, 2, 8-10 or 13-20 or a product of any of claims 3-7, 11, 12 or 18-20 wherein $p = 1$.

22. A method of any of claims 1, 2, 8-10 or 13-21 or a product of any of claims 3-7, 11, 12 or 18-21 wherein $q = 1, 2$ or 3 .

5 23. A method of any of claims 1, 2, 8-10 or 13-22 or a product of any of claims 3-7, 11, 12 or 18-22 wherein $q = 1$.

24. A method of any of claims 1, 2, 8-10 or 13-23 or a product of any of claims 3-7, 11, 12 or 18-23 wherein $n = 2$, $m = 1$, $p = 1$ and $q = 1$, such that the ion of formula (I) has the structure:

Formula (I)	$\begin{array}{c} \text{Ar}^2 \\ \\ \text{Ar}^2-\text{C}-\text{Ar}^1-\text{L}_M\text{M}'-\text{B}_P' \\ \star \end{array}$
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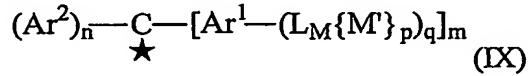
25. A method of any of claims 1, 2, 8-10 or 13-24 or a product of any of claims 3-7, 11, 12 or 18-24 wherein the biopolymer is a polymer found in biological samples.

26. A method or product of claim 25 wherein the biopolymer is a polypeptide, polysaccharide, or 15 polynucleotide.

27. A method or product of claim 26 wherein the biopolymer is a polypeptide.

28. A method or product of any of claims 25-27 wherein the biopolymer does not readily form a 20 molecular ion on illumination of laser light at 340 nm.

29. A method of any of claims 1, 2, 8-10 or 13-28 or a product of any of claims 3-7, 11, 12 or 18-28 wherein the ratio $m(\text{B}_P') / m(\text{IX})$ is more than 2, where $m(\text{IX})$ is the mass of the fragment (IX)



25 of the cation of formula (I) and $m(\text{B}_P')$ is the mass of the biopolymer residue B_P' .

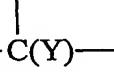
30. A method of any of claims 1, 2, 8-10 or 13-29 or a product of any of claims 3-7, 11, 12 or 18-29 wherein M is: $-\text{NR}_2$; $-\text{SR}$; $-\text{OR}$; $-\text{B}(\text{R})\text{Y}$; $-\text{BY}_2$; $-\text{C}(\text{R})_2\text{Y}$; $-\text{C}(\text{R})\text{Y}_2$; $-\text{CY}_3$; $-\text{C}(=\text{Z})\text{Y}$;

-Z-C(=Z)Y; -C(=Z)R; -C(R)(OH)OR; -C(R)(OR)₂; -S(=O)Y; -Z-S(=O)Y; -S(=O)₂Y; -Z-S(=O)₂Y; -S(=O)₃Y; -Z-S(=O)₃Y; -P(=Z)(ZR)Y; -P(=Z)Y₂; -Z-P(=Z)(ZR)Y; -Z-P(=Z)Y₂; -P(=Z)(R)Y; -Z-P(=Z)(R)Y; or -N=C(=Z), where Y is independently a leaving group, Z is independently O, S or N(R) and R is independently H, C₁₋₈hydrocarbyl or C₁₋₈hydrocarbyl substituted with one or more A.

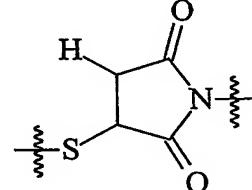
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31. A method of any of claims 1, 2, 8-10 or 13-29 or a product of any of claims 3-7, 11, 12 or 18-29 wherein M is: -N(R)-; -S-; -O-; -B(Y)-; -C(R)(Y)-; -CY₂-; -C(=O)-; -C(OH)(OR)-; or -C(OR)₂-, where Y is independently a leaving group and R is independently H, C₁₋₈hydrocarbyl or C₁₋₈hydrocarbyl substituted with one or more A.

10

32. A method of any of claims 1, 2, 8-10 or 13-29 or a product of any of claims 3-7, 11, 12 or 18-29 wherein M is:  C(Y), where Y is a leaving group.

33. A method of any of claims 1, 2, 8-10 or 13-29 or a product of any of claims 3-7, 11, 12 or 18-29 wherein the covalent linkage is selected from those produced through the reaction of one the

following groups: -CO-NH-; biotin-(strept)avidin;  ; or -NH-CS-NH-.

34. A method of any of claims 1, 2, 8-10 or 13-33 or a product of any of claims 3-7, 11, 12 or 18-33 wherein L_M is O or S.

20

35. A method of any of claims 1, 2, 8-10 or 13-33 or a product of any of claims 3-7, 11, 12 or 18-33 wherein L_M is -E^M-, -(D^M)_t-, -(E^M-D^M)_t-, -(D^M-E^M)_t-, -E^M-(D^M-E^M)_t- or -D^M-(E^M-D^M)_t- (in the orientation Ar¹-(L_M{M})_p)_q or Ar¹-(L_M{M'})_p)_q, as appropriate),

where:

25 a sufficient number of linking covalent bonds, in addition to the covalent bonds at the chain termini shown, are provided on groups E^M and D^M for linking the p instances of M (or M') groups;

D^M is independently C₁₋₈hydrocarbylene or C₁₋₈hydrocarbylene substituted with one or more A;

E^M (in the orientation Ar¹-(L_M{M})_p)_q or Ar¹-(L_M{M'})_p)_q, as appropriate) is independently -Z^M-; -C(=Z^M)-; -Z^MC(=Z^M)-; -C(=Z^M)Z^M-; -Z^MC(=Z^M)Z^M-; -S(=O)-; -Z^MS(=O)-; -S(=O)Z^M-;

-Z^MS(=O)Z^M-, -S(=O)Z^M-, -Z^MS(=O)Z^M-, -S(=O)Z^M-, -Z^MS(=O)Z^M-, where Z^M is independently O, S or N(R^M) and where R^M is independently H, C₁₋₈hydrocarbyl (e.g. C₁₋₈alkyl) or C₁₋₈hydrocarbyl substituted with one or more A; and

$t = 1$ or more.

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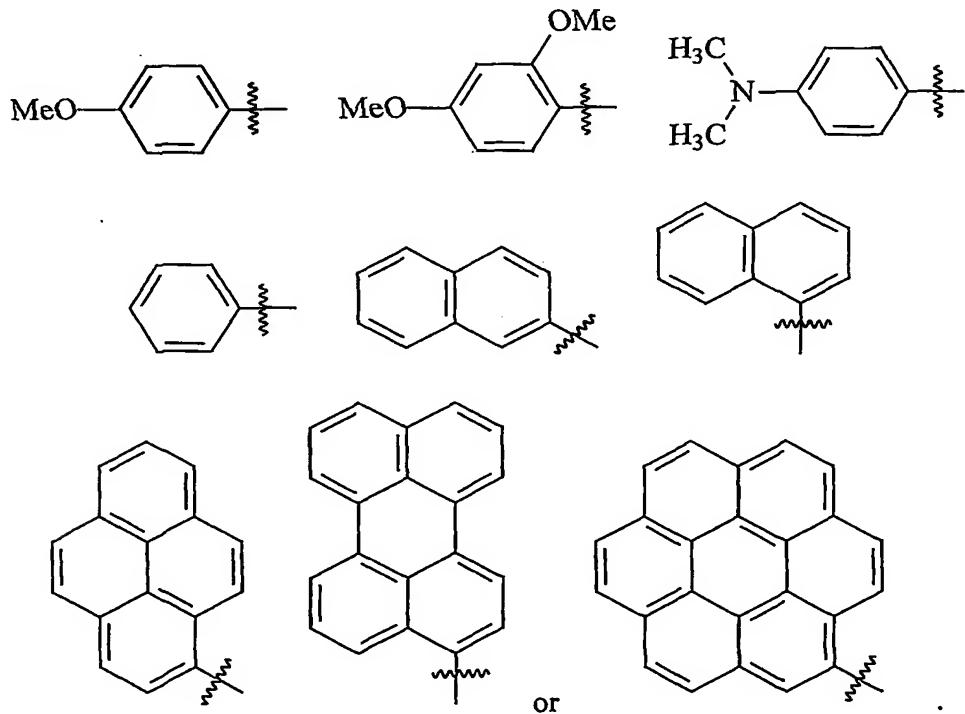
36. A method of any of claims 1, 8, 10 or 13-35 or a product of any of claims 3, 6, 11, 12 or 18-35 wherein the group X is halogen, hydroxy, C₁₋₈hydrocarbyloxy, C₁₋₈hydrocarbyloxy substituted with one or more A, C₁₋₈heterohydrocarbyloxy, C₁₋₈heterohydrocarbyloxy substituted with one or more A, mesyl, tosyl, pentafluorophenyl, -O-succinimidyl -S-succinimidyl, or phenyloxy substituted with one or more A.

10 with one or more A.

37. A method of any of claims 1, 2, 8-10 or 13-36 or a product of any of claims 3-7, 11, 12 or 18-36 wherein Ar^2 is independently cyclopropyl, cyclopropyl substituted with one or more A, aryl, aryl substituted with one or more A, heteroaryl, or heteroaryl substituted with one or more A.

15

38. A method of any of claims 1, 2, 8-10 or 13-37 or a product of any of claims 3-7, 11, 12 or 18-37 wherein Ar^2 is



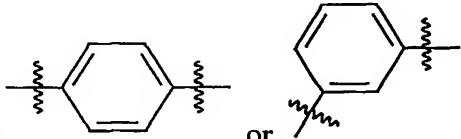
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39. A method of any of claims 1, 2, 8-10 or 13-38 or a product of any of claims 3-7, 11, 12 or 18-38 wherein Ar^1 is independently cyclopropylene, cyclopropylene substituted with one or more A, arylene, arylene substituted with one or more A, heteroarylene, or heteroarylene substituted with one or more A.

5

40. A method of any of claims 1, 2, 8-10 or 13-39 or a product of any of claims 3-7, 11, 12 or

18-39 wherein Ar^1 is



41. A method of any of claims 1, 2, 8-10 or 13-40 or a product of any of claims 3-7, 11, 12 or
10 18-40 wherein L^5 is O or S.

42. A method of any of claims 1, 2, 8-10 or 13-40 or a product of any of claims 3-7, 11, 12 or 18-40 wherein L^5 is $-E^5-$, $-(D^5)_{t^1}-$, $-(E^5-D^5)_{t^1}-$, $-(D^5-E^5)_{t^1}-$, $-E^5-(D^5-E^5)_{t^1}-$ or $-D^5-(E^5-D^5)_{t^1}-$,

where:

15 D^5 is independently C_{1-8} hydrocarbylene or C_{1-8} hydrocarbylene substituted with one or more A;

E^5 is independently $-Z^5-$, $-C(=Z^5)-$, $-Z^5C(=Z^5)-$, $-C(=Z^5)Z^5-$, $-Z^5C(=Z^5)Z^5-$, $-S(=O)-$, $-Z^5S(=O)-$, $-S(=O)Z^5-$, $-Z^5S(=O)Z^5-$, $-S(=O)_2-$, $-Z^5S(=O)_2-$, $-S(=O)_2Z^5-$, $-Z^5S(=O)_2Z^5-$, where Z^5 is independently O, S or $N(R^5)$ and where R^5 is independently H, C_{1-8} hydrocarbyl or C_{1-8} hydrocarbyl
20 substituted with one or more A; and

$t^1 = 1$ or more.